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(54) Title: HIGH TEMPERATURE ALLOYS

(57) Abstract: An improved nickel-chromium-iron alloy is provided, which comprises up to about 5% of hafnium-containing particles. In one embodiment, an improved creep resistant castable oxide dispersion strengthened nickel-chromium-iron alloy comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles. Further embodiments of the improved alloy can comprise additionally up to about 15% by weight aluminium. The alloy is particularly useful in the production of creep resistant tubes and castings, for example, for the petrochemical market.

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### High temperature Alloys

This invention relates to high temperature alloys, and more particularly to oxide dispersion strengthened alloys  
5 having improved creep resistance and carburisation resistance at high temperatures.

Frequently high temperature alloys used, for example, in the manufacture of alloy tubes for steam methane  
10 reforming, suffer from insufficient creep resistance. In other applications of high temperature alloys, for example, alloy tubes used in ethylene pyrolysis, the alloys suffer from insufficient carburisation resistance and, in consequence, insufficient creep resistance.

15 The petrochemical industry continues to look for improved materials and other technologies capable of withstanding increasingly demanding process conditions to enable more efficient production and achieve enhanced yields. In the case of steam methane reforming, these conditions involve higher temperatures and higher gas pressures. In the case of ethylene pyrolysis, the conditions involve increasingly severe pyrolysis/cracking conditions (higher temperatures, shorter residence times, and lower partial  
20 pressures of product). Currently available alloys have specific deficiencies that cause relatively early failure under these process conditions. This is the case presently for both castable alloy tubes and wrought alloy tubes.

30 An example of a known alloy material is INCOLOY® alloy 803 (UNS S 35045), which is an iron-nickel-chromium alloy specifically designed for use in petrochemical, chemical and thermal processing applications. The composition of  
35 INCOLOY 803, by weight, is 25%Cr, 35%Ni, 1%Mn, 0.6%Ti,

0.5%Al, 0.7%Si, 0.07%C and balance Fe. Relatively unsuccessful efforts have been made to improve the properties of this alloy by the addition of further alloying components and also by cladding.

5

It has been known for about thirty years that alloy creep resistance can be considerably improved by adding a fine dispersion of oxide particles into a metallic matrix, yielding a so-called oxide dispersion strengthened (ODS) alloy. Such alloys exhibit a creep threshold, that is to say, below a certain stress their creep rate is very low. This behaviour is commonly explained by interfacial pinning of the moving dislocations at the oxide particle; Bartsch, M., A. Wasilkowska, A. Czyrska-Filemonowicz and U. Messerschmidt *Materials Science & Engineering A* **272**, 152-162 (1999). It has recently been proposed to provide oxide dispersion strengthened clad tubes based on INCOLOY 803, but to date no entirely successful commercial product is available

20 [www.oit.doe.gov/imf/factsheets/mtu tubes](http://www.oit.doe.gov/imf/factsheets/mtu_tubes)).

The nickel-chromium-iron alloys in the ethylene pyrolysis market which have been produced to have good corrosion resistance and acceptable creep resistance mainly develop an oxide coating layer based on chromium oxide (with in some cases admixed silica). This layer under excessively carburising service conditions (high temperature, high carbon activity, low oxygen pressure) can become destabilised and is then no longer a functional carbon diffusion barrier. Alumina is known to be a very stable oxide and ideally it would be desirable to create an alumina layer on the surface of the nickel-chromium-iron alloy, for example, by adding aluminium to the melt. However, aluminium has two highly detrimental effects on the mechanical properties of such alloys and especially

on the creep resistance. Firstly, addition of aluminium to the melt can produce a dispersion of alumina in the alloy that can drastically reduce the creep resistance properties. Secondly, aluminium can form brittle Ni-Al phases in the alloy.

It will be apparent that there is a need for new high temperature alloys with improved properties for a variety of high temperature applications.

According to the present invention there is provided a new class of improved nickel-chromium-iron alloys comprising hafnium and methods for their production.

In a first aspect, the invention provides an improved creep resistant nickel-chromium-iron alloy comprising up to about 5% by weight of hafnium-containing particles.

In a second aspect, the invention provides an improved oxide dispersion strengthened nickel-chromium-iron alloy which comprises up to about 5% by weight of hafnium, with at least part of the hafnium being present as finely divided oxidised particles.

In a third aspect, the invention provides a corrosion resistant nickel-chromium-iron-aluminium alloy comprising up to about 15%, preferably up to about 10%, by weight of aluminium and up to about 5% by weight of hafnium-containing particles.

The alloys of the invention are castable and can be formed into tubes and coils.

In a further aspect, the present invention provides an oxide dispersion strengthened castable alloy comprising,

by weight:

	Carbon	0.01 - 0.7%
	Silicon	0.1 - 3.0%
5	Manganese	0 - 3.0%
	Nickel	15 - 90%
	Chromium	5 - 40%
	Molybdenum	0 - 3.0%
	Niobium	0 - 2.0%
10	Tantalum	0 - 2.0%
	Titanium	0 - 2.0%
	Zirconium	0 - 2.0%
	Cobalt	0 - 2.0%
	Tungsten	0 - 4.0%
15	Hafnium	0.01 - 4.5%
	Aluminium	0 - 15%
	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	balance	iron and incidental impurities,

20

with the proviso, that at least one carbide forming element whose carbide is more stable than chromium carbide selected from niobium, titanium, tungsten, tantalum and zirconium is present and that at least part  
25 of the hafnium is present as finely divided oxide particles.

A preferred embodiment of an oxide dispersion  
30 strengthened nickel-chromium-iron castable alloy according to the invention comprises; by weight:

	Carbon	0.01 - 0.5%
	Silicon	0.01 - 2.5%
35	Manganese	0 - 2.5%

	Nickel	15 - 50%
	Chromium	20 - 40%
	Molybdenum	0 - 1.0%
	Niobium	0 - 1.7%
5	Titanium	0 - 0.5%
	Zirconium	0 - 0.5%
	Cobalt	0 - 2.0%
	Tungsten	0 - 1.0%
	Hafnium	0.01 - 4.5%
10	Aluminium	0 - 15%
	balance iron and incidental impurities,	

with the proviso, that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

Preferred alloy compositions according to the invention include the following:

20	Carbon	0.3 to 0.7%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	30 to 40%
	Chromium	20 to 30%
25	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
30	Cobalt	2.0% max.
	Tungsten	1.0% max.
	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	Balance iron and incidental impurities.	

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	Carbon	0.03 to 0.2%
	Silicon	0.1 to 0.25%
	Manganese	2.5% max.
	Nickel	30 to 40%
5	Chromium	20 to 30%
	Molybdenum	3.0% max.
	Niobium	1.7% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
10	Zirconium	0.5% max.
	Cobalt	2.05% max.
	Tungsten	1.0% max.
	Aluminium	0 - 15.0%
	Nitrogen	0.001 - 0.5%
15	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

	Carbon	0.3 to 0.7%
	Silicon	0.01 to 2.5%
20	Manganese	2.5% max.
	Nickel	40 to 60%
	Chromium	30 to 40%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
25	Hafnium	0.01 to 4.5%
	Titanium	1.0% max.
	Zirconium	1.0% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.,
30	Aluminium	0 - 15.0%
	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

	Carbon	0.03 to 0.2%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	40 to 50%
5	Chromium	30 to 40%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
10	Zirconium	0.5% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.,
	Aluminium	0 - 15.0%
	Nitrogen	0.001 - 0.5%
15	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

	Carbon	0.3 to 0.7%
	Silicon	0.01 to 2.5%
20	Manganese	2.5% max.
	Nickel	19 to 22%
	Chromium	24 to 27%
	Molybdenum	3.0% max.
	Niobium	2.0% max
25	Hafnium	0.01 to 4.5%
	Cobalt	2.0% max.
	Tungsten	1.0% max.,
	Aluminium	0 - 15.0%
	Nitrogen	0.001 - 0.5%
30	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

	Carbon	0.03 to 0.2%
35	Silicon	0.1 to 2.5%



	Manganese	2.5% max
	Nickel	30 to 45%
	Chromium	19 to 22%
	Molybdenum	3.0% max.
5	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.0% max.
10	Tungsten	1.0% max.,
	Aluminium	0 - 15.0%
	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

15

Other preferred nickel-chromium-iron castable alloys according to the invention include the following compositions, where all percentages are given by weight:

20

	Carbon	Silicon	Manganese	Nickel	Chromium	Molybdenum
A	0.3 - 0.5	0.1 - 2.5	2.5 max	30 - 40	20 - 30	1.0 max
B	0.03 - 0.2	0.1 - 2.5	2.5 max	30 - 40	20 - 30	1.0 max
C	0.3 - 0.6	0.1 - 2.5	2.5 max	40 - 60	30 - 40	1.0 max
D	0.03 - 0.2	0.1 - 2.5	2.5 max	40 - 60	30 - 40	1.0 max
E	0.30 - 0.5	0.1 - 2.5	2.5 max	19 - 22	24 - 27	1.0 max
F	0.03 - 0.2	0.1 - 2.5	2.5 max	30 - 45	19 - 22	1.0 max

	Niobium	Hafnium	Optional Aluminium	Titanium	Zirconium	Cobalt	Tungste
A	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max
B	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max

C	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max
D	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max
E	2 max	0.025 - 4.5	6.0 max			2.0 max	1.0 max
F	2 max	0.025 - 4.5	6.0 max	0.5 max	0.5 max	2.0 max	1.0 max

balance iron and incidental impurities.

The amount of hafnium in the alloy, by weight, is preferably from 0.05 to 3.0%, more preferably from 0.1% to 1.0% and most preferably from 0.2 to 0.5% for the high carbon alloy (0.3 - 0.6% carbon), and more than 1% for the low carbon alloy (0.03 - 0.2% carbon), preferably from 1% to 4.5%. Preferably the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less, more preferably from 5 microns to 0.25 microns or less.

Examples of particularly preferred alloy compositions according to the invention consist essentially of the following components, by weight:

	Carbon	0.45%
20	Silicon	1.3%
	Manganese	0.9%
	Nickel	33.8%
	Chromium	25.7%
	Molybdenum	0.03%
25	Niobium	0.85%
	Hafnium	0.25%
	Titanium	0.1%
	Zirconium	0.01%
	Cobalt	0.04%
30	Tungsten	0.01%
	Nitrogen	0.1%

	Iron	balance.
	Carbon	0.07%
5	Silicon	1.0%
	Manganese	0.98%
	Nickel	32.5%
	Chromium	25.8%
	Molybdenum	0.20%
10	Niobium	0.04%
	Hafnium	1.1%
	Titanium	0.12%
	Zirconium	0.01%
	Cobalt	0.04%
15	Tungsten	0.08%
	Nitrogen	0.1%
	Iron	balance.
	Carbon	0.34%
20	Silicon	1.68%
	Manganese	1.10%
	Nickel	32.0%
	Chromium	21.3%
	Molybdenum	0.01%
25	Niobium	0.80%
	Hafnium	0.25%
	Titanium	0.12%
	Zirconium	0.01%
	Aluminium	3.28%
30	Cobalt	0.04%
	Tungsten	0.01%
	Iron	balance,
	Carbon	0.42%
35	Silicon	1.79%

	Manganese	1.17%
	Nickel	33.2%
	Chromium	23.3%
	Molybdenum	0.02%
5	Niobium	0.77%
	Hafnium	0.24%
	Titanium	0.10%
	Zirconium	0.01%
	Aluminium	1.64%
10	Cobalt	0.04%
	Tungsten	0.08%
	Iron	balance.

15 Incidental impurities in the alloys of the invention can comprise, for example, phosphorus, sulphur, vanadium, zinc, arsenic, tin, lead, copper and cerium, up to a total amount of about 1.0%.

20 In a still further aspect, the invention provides a method of manufacturing an oxide dispersion strengthened castable nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.

25 To manufacture the alloys of the invention, it is important to provide conditions in the melt which permit oxidation of the hafnium particles without allowing detrimental reactions which would result in the hafnium  
30 (with or without aluminium) being taken up in the slag. The correct oxidising conditions can be achieved by appropriate adjustment or additions of the components, example, silicon and/or manganese, and by ensuring that unwanted contaminants are absent or kept to a minimum. If  
35 the slag is able to react with the oxidised hafnium

particles this of course removes them detrimentally from the melt. The level of oxygen in the melt can be varied by additions of, for example, one or more of silicon, niobium, titanium, zirconium, chromium, manganese, calcium and the optimum free oxygen level necessary to react with the hafnium particles can readily be found by routine experimentation.

In the manufacture of the castable nickel-chromium-iron alloys of the invention, it is often desirable to introduce micro-additions of certain components to obtain the desired alloy properties. Such components can be very reactive with oxygen, but in general less reactive than hafnium. Formation of oxides by these micro-additions should be avoided, and preferably the added components should form carbides, carbonitrides, or nitrides, or stay in solid solution. Preferably any such micro-additions are made after the addition of hafnium. For example, after the reaction of the hafnium particles with free oxygen, alloying amounts of titanium and/or zirconium may be added, up to the specified limits of 0.5% by weight in each case. The substantial removal of available free oxygen from the melt helps to ensure that any such titanium and/or zirconium additions do not form oxides, which could react detrimentally with the hafnium particles and reduce the yields of titanium, zirconium and hafnium present in the alloy.

It is important that the hafnium is added to the melt as finely divided particles and that it is oxidised in situ.

We have discovered that hafnium added to nickel/chromium alloys in non-particulate form does not disperse, or reacts only with the carbon/nitrogen present resulting in a decrease of the alloy properties. Attempts to add

large pieces of hafnium to nickel/chromium micro-alloys have revealed that the hafnium does not disperse, but settles to the bottom of the alloy melt, and so is not present in the final casting. Surprisingly, we have also  
5 found that the addition of hafnia (hafnium oxide) particles directly to the melt does not provide the desired dispersion strengthening either. Hafnia added in this way simply goes into the slag. According to the invention it has been found that it is necessary to carry  
10 out the oxidation of the hafnium particles in the melt in order to obtain the desired improvements.

The charge make up can be a virgin charge (pure metals), a mixture of virgin charge and reverts, a mixture of  
15 virgin charge and ingots, or a mixture of virgin charge and reverts and ingots. The ingots can be made from argon/oxygen decarburisation (AOD) revert alloy treatment or from in-house reverts treated, for example, by argon purging. In each case the chemical composition of the  
20 melt should be carefully monitored to avoid contaminants and the formation of unwanted slag.

Special care should be taken to deslag the bath, and the maximum amount of slag is preferably removed from the  
25 surface of the bath. It is possible to improve slag removal by the use of a neutral deslag powder. If desired the melt can be maintained in an argon atmosphere, but this is not essential.

30 The melt temperature is preferably in the range of from 1500°C to 1700 °C, preferably from 1610 °C to 1670 °C for nickel-chromium-Iiron, and 1630°C to 1690C for nickel-chromium-iron-aluminium.

Hafnium particles are preferably added to the melt just before pouring the molten alloy into the mould. If a ladle is used, the hafnium is preferably added in the ladle. To improve the hafnium dispersion, the molten alloy is preferably stirred before pouring.

Any type of hafnium can be used, but electrolytic hafnium is preferred. The hafnium particles are preferably reduced in size as much as possible, for example, by grinding to a fine powder in a suitable mill. The hafnium particles preferably have a particle size of less than 5 mm, preferably less than 4 mm, with an average particle size of from 1 to 2 mm. When dispersed in the melt, the hafnium particles are further reduced in size.

15

The high carbon alloys of the invention (0.3 - 0.6% carbon) have a primary carbide network similar to the corresponding alloys without the oxide dispersion. The primary carbides are mainly composed of chromium and/or iron carbo-nitrides, optionally with niobium, titanium and/or zirconium carbo-nitrides also present. The invention also provides the possibility of obtaining a dispersion of secondary carbides after the alloy has been brought to a high temperature. These secondary carbides are mainly chromium (or other elements such as iron) carbo-nitrides and optionally niobium, titanium (and/or zirconium) carbo-nitrides.

The low carbon alloys of the invention (0.03 - 0.2% carbon) can contain a dispersion of carbides, carbo-nitrides, or nitrides, for example; titanium nitrides, titanium carbo-nitrides, niobium carbides, niobium carbo-nitrides, niobium nitrides, zirconium nitrides, zirconium carbo-nitrides, zirconium carbides; tantalum carbides, tantalum carbo-nitrides, tantalum nitrides, tungsten

carbides, tungsten nitrides, and/or tungsten carbo-nitrides.

In additions to these precipitates, the invention  
5 provides for the formation of a hafnia / hafnium oxide  
dispersion (the hafnium can be oxidised to form  $\text{HfO}_2$ , but  
it can be expected that there will also be formed an  
oxide  $\text{HfO}_x$  with  $x$  as a variable). Furthermore, in alloys  
10 containing more than a trace of niobium and titanium, for  
example, high carbon nickel-chromium-iron alloys,  
hafnium/niobium/titanium carbo-nitrides and (rarely)  
oxides mixtures (wherein the quantities of niobium and  
titanium are variable as well as the quantities of  
15 nitrogen and oxygen) can be expected to be present. Also,  
more numerous titanium nitride (and/or carbide)  
dispersions may be observed in the alloy, some of which  
may also contain hafnia particles. It is also possible  
that some hafnium carbo-nitrides may be formed.

20 According to another aspect of the invention, there is  
provided an oxide dispersion strengthened nickel-  
chromium-iron alloy which comprises up to about 5% by  
weight of hafnium, with at least part of the hafnium  
being present as finely dispersed oxidised particles, the  
25 alloy having a carbon content of from 0.3% to 0.5% by  
weight and having improved high temperature creep  
resistance, leading to an improved service life  
expectancy. Without wishing to be confined to any  
particular theory, it is believed that the creep  
30 resistance of such high carbon alloys, in the substantial  
absence of aluminium, derives from the ability of the  
particle dispersion to delay the motion of the  
dislocations in the alloy lattice. In the case of a  
micro-alloy, without the oxide dispersion, the motion of  
35 dislocations can be delayed by the presence of carbide



(and/or nitride) precipitates, but the presence of the oxide dispersion provides a substantial unexpected extra improvement. An example of a high carbon oxide dispersion strengthened alloy is alloy A in Table 1 (wherein aluminium is absent).

In a still further aspect, the invention provides an oxide dispersion strengthened nickel-chromium-iron alloy, which comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles, the alloy having a carbon content of from 0.03% - 0.2%, preferably 0.03% - 0.1%, more preferably 0.03% - 0.08%, for example, about 0.05% - 0.07%, and a significantly increased service temperature, preferably greater than 1150°C. Without wishing to be confined to any particular theory, it is believed that the improved high temperature performance of the new low carbon alloys of this further aspect of the invention is due to the replacement of the strengthening carbide dispersion by a hafnia dispersion which is more stable than the carbide at high temperature. An example of a low carbon oxide dispersion strengthened alloy is alloy B in Table 1 (wherein aluminium is absent).

Where the nickel-chromium-iron alloy of the invention also comprises aluminium, the aluminium is preferably present in an amount of from 0.1% to 10% by weight, more preferably from 0.5% to 6% by weight and most preferably from 1.0 to 5% by weight.

In a still further aspect of the invention, there is provided a method of manufacturing a carburisation resistant nickel-chromium-iron alloy which comprises adding sequentially finely divided hafnium particles and aluminium to a melt of the alloy before pouring.

Preferably the aluminium is added to the melt immediately before pouring the molten alloy into the mould.

5 Without wishing to be confined by any particular theory, it is believed that the addition of hafnium limits the amount of available oxygen in the alloy able to react with the aluminium and minimises or eliminates the formation of a detrimental dispersion of alumina  
10 particles.

The alloys of the invention can be formed into tubes, for example, by rotational moulding, and such rotationally moulded tubes are a further aspect of the invention. The  
15 rotational moulding process can provide a non-uniform particle distribution in the tube wall, with the greater concentration of particles being towards the outer surface of the tube wall, and this can be beneficial in some cases. For example, in certain applications the  
20 internal bore of the tube is machined, removing 4-5 mm of material; this gradient of concentration ensures that the hafnium/hafnia reinforcement is kept in the useful part of the tube. Other components that can be manufactured from the new alloys include fittings, fully fabricated  
25 ethylene furnace assemblies, reformer tubes and manifolds.

For high chromium content (more than 10%) alloys, a further advantage of the hafnium addition is that it can  
30 tend to improve the oxide layer adherence at the surface of an alloy tube. For example, where nickel-chromium-iron alloys are used in ethylene furnaces, they are able to develop an oxide layer on the surface that protects the alloy against corrosion by carburisation. This  
35 protective oxide layer is formed ideally of

chromium/manganese/silicon oxides, but can also include iron and nickel oxides. The oxide layer has a tendency to spall during the tube service life (because of differences of coefficients of expansion with the alloy, compressive stresses in the oxide, etc). Spalling leaves the alloy unprotected against corrosion from the gaseous and particulate reactants of the ethylene cracking process. It has surprisingly been found that the addition of hafnium as described herein can tend to delay the spalling of the protective oxide layer.

Embodiments of alloys according to the invention are illustrated in the accompanying Drawings, by way of example only, in which:

15

Figure 1 is a photomicrograph of a first alloy according to the invention with its composition by weight;  
Figure 2 is a photomicrograph of a second alloy according to the invention with its composition by weight;  
Figure 3 is a photomicrograph of a third alloy according to the invention with its composition by weight;  
Figure 4 is a photomicrograph of a fourth alloy according to the invention with its composition by weight;  
Figure 5 is a photomicrograph of a fifth alloy according to the invention; and  
Figure 6 is a photomicrograph of a sixth alloy according to the invention.

The invention is further illustrated by the following Examples, in which all percentages are by weight:

30

#### Example 1

The following melt composition is produced in a clean furnace:

35

	Nickel	35%
	Chromium	25%
	Carbon	0.4%
5	Niobium	0.8 - 0.9%
	Silicon	1.6 - 1.8%
	Manganese	1.1 - 1.3%
	Iron	balance.

10 The temperature of the melt is raised to a tap temperature of from 1640°C to 1650°C and the silicon content checked to obtain the correct oxidising conditions. The furnace is then de-slaged, removing as much slag as possible. 100kg of alloy are then tapped  
15 into a ladle and 0.35% hafnium particles of particle size maximum 5 mm, average 1 to 2 mm, are added to the tap stream. After the hafnium addition, 0.18% titanium, in the form of FeTi is added to the ladle.

20 The alloy in the ladle is stirred and immediately poured into a tube mould.

The creep resistance properties of the alloy thus produced were compared with the properties of an  
25 otherwise identical commercial alloy without hafnium.

The results of a Larson-Miller plot of the stress-rupture properties of the commercial alloy derived from the regression analysis of numerous creep tests gave a  
30 typical figure of 16.7 MPa at a temperature of 1100°C (Figure 7). The commercial alloy is expected to fail after a minimum of 100 hours, with a mean value failure of 275 hours. The alloy according to the invention had a minimum failure time of rupture of 370 hours and a mean  
35 value failure of 430 hours. The creep strength

20

comparison is shown in Figure 8.

The results of a 100,000 hour creep rupture stress test for the alloy of Example 1 are given in Table 1:

5

Table 1

**CREEP RUPTURE STRESS 100,000H LIFE FOR ALLOY EXAMPLE 1:**

**N/mm<sup>2</sup> (psi)**  
10

	900	950	1000	1050	1100
<b>MEAN</b>	<b>33.86</b>	<b>23.15</b>	<b>14.70</b>	<b>8.67</b>	<b>4.75</b>
	<b>(4929)</b>	<b>(3374)</b>	<b>(2148)</b>	<b>(1273)</b>	<b>(704)</b>
15					
<b>Minimum</b>	<b>31.37</b>	<b>21.44</b>	<b>13.62</b>	<b>8.03</b>	<b>4.40</b>
	<b>(4567)</b>	<b>(3126)</b>	<b>(1991)</b>	<b>(1180)</b>	<b>(653)</b>

20

**Example 2**

The procedure of Example 1 is repeated using the same melt composition except that the titanium addition is  
25 omitted.

The creep resistance properties of the alloy thus produced were compared with the properties of an otherwise identical commercial alloy from which the  
30 hafnium addition was omitted.

The results of a Larson-Miller plot of the stress-rupture properties of the commercial alloy derived from the regression analysis of numerous creep tests gave a

typical figure of 16.2 MPa at a temperature of 1100°C. The commercial alloy is expected to fail after a minimum of 100 hours, with a mean value failure of 202 hours. The alloy according to the invention had a minimum  
5 failure time of rupture of 396 hours, a mean value failure of 430 hours and a maximum failure time of rupture of 629 hours.

The results of Examples 1 and 2 show the dramatic  
10 improvement in creep properties that can be obtained using the alloys and method of the invention.

### Example 3

15 This example describes the production of a low carbon oxide dispersion strengthened alloy according to the invention.

The following melt composition is produced in a clean  
20 furnace:

Nickel	33% - 35%
Chromium	24% - 26%
Carbon	0.04% - 0.08%
25 Silicon	1.0% - 1.2%
Manganese	1.0% - 1.2%
Molybdenum	0.14% - 0.3%
Iron	balance.

30 The temperature of the melt is raised to a tap temperature of from 1640°C to 1650°C and the silicon content checked. The furnace is then de-slaged, removing as much slag as possible. 100kg of alloy are then tapped into a ladle and 0.75% hafnium particles of particle size  
35 maximum 5 mm, average 1 - 2 mm, are added to the tap

stream. After the hafnium addition, 0.25% titanium, in the form of FeTi is added to the ladle.

The alloy in the ladle is stirred and immediately poured  
5 into a tube mould. The chemical composition of the tube alloy by spectrometer analysis is:

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti
0.07	1.0	0.91	32.9	25.5	0.20	0.03	0.30	0.17

Zr	Co	W
0.01	0.03	0.06

10

Traces ( P+ S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.24

A photomicrograph of the alloy is shown in Figure 5. The dispersed oxidised particles can clearly be seen.

15

#### Example 4

The procedure of Example 3 is repeated using the same melt composition except that the hafnium addition is  
20 0.5%. The chemical composition of the tube alloy by spectrometer analysis is:

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti
0.07	1.00	0.98	32.5	25.8	0.02	0.04	0.50	0.12

Zr	Co	W
0.01	0.04	0.08

25

Traces ( P+ S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.23

A photomicrograph of the alloy is shown in Figure 6. The dispersed oxidised particles can clearly be seen.

- 5 Examples 3 and 4 show a higher solidus than the high carbon alloys of Examples 1 and 2, indeed their solidus is 1344°C instead of 1260°C for the high carbon alloys.

#### Example 5

10

This Example describes the production of an oxide dispersion strengthened nickel-chromium-iron alloy according to the invention comprising both hafnium and aluminium.

15

A nickel-chromium-iron alloy melt having the following constituents by weight is formed in a clean furnace and brought to tapping temperature.

20	Nickel	35%
	Chromium	25%
	Carbon	0.4%
	Niobium	0.8 - 0.9%
	Silicon	1.6 - 1.8%
25	Manganese	1.1 - 1.3%
	Iron	balance.

Once the appropriate oxidising conditions have been obtained, 100Kg of the melt is tapped into a ladle, whilst at the same time adding hafnium particles to the tap stream to give a hafnium level of 0.15% to 0.30% by weight in the alloy. Immediately before pouring aluminium is added to the melt to give an aluminium level of 1.5% to 1.8%.

35



The alloy of Example 5 has been tested to confirm that aluminium can improve the carburisation resistance of a hafnium-containing alloy according to the invention. A very severe pack-carburisation test was performed, the results of which are shown in Figure 9. The creep resistance of the alloy was found to be substantially maintained compared to an identical alloy without hafnia and aluminium additions. Indeed only a decrease of maximum 20% in creep resistance was observed compared to an identical alloy without hafnium and aluminium additions. On the other hand, an identical alloy with an aluminium addition, but without hafnium, showed a decrease in creep resistance of 80%.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features  
5 disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

## CLAIMS

1. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

5

Carbon 0.01 - 0.7%

Silicon 0.1 - 3.0%

Manganese 0 - 2.5%

Nickel 15 - 90%

10 

Chromium 5 - 40%

Molybdenum 0 - 3.0%

Niobium 0 - 2.0%

Tantalum 0 - 2.0%

Titanium 0 - 2.0%

15 

Zirconium 0 - 2.0%

Cobalt 0 - 2.0%

Tungsten 0 - 4.0%

Hafnium 0.01 - 4.5%

Aluminium 0 - 15%

20 

Nitrogen 0.001 - 0.5%

Oxygen 0.001 - 0.7%

balance iron and incidental impurities,

with the proviso, that at least one carbide forming  
25 element whose carbide is more stable than chromium  
carbide selected from niobium, titanium, tungsten,  
tantalum and zirconium is present and that at least part  
of the hafnium is present as finely divided oxide  
particles.

30

2. An oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

Carbon 0.01 to 0.5%

35 

Silicon 0.01 to 2.5%

	Manganese	0 to 2.5%
	Nickel	15 to 50%
	Chromium	20 to 40%
	Molybdenum	0 to 1.0%
5	Niobium	0 to 1.7%
	Titanium	0 to 0.5%
	Zirconium	0 to 0.5%
	Cobalt	0 to 2.0%
	Tungsten	0 to 1.0%
10	Hafnium	0.01 to 4.5%,

balance iron and incidental impurities,

15 with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxide particles.

3. An alloy according to claim 1 having the following composition, by weight:

20

	Carbon	0.3 to 0.7%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	30 to 40%
25	Chromium	20 to 30%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
30	Zirconium	0.5% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.
	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
35	Balance iron and incidental impurities.	

4. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.03 to 0.2%
5	Silicon	0.1 to 0.25%
	Manganese	2.5% max.
	Nickel	30 to 40%
	Chromium	20 to 30%
	Molybdenum	3.0% max.
10	Niobium	1.7% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.05% max.
15	Tungsten	1.0% max.
	Aluminium	0 - 15.0%
	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

20

5. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.3 to 0.7%
25	Silicon	0.01 to 2.5%
	Manganese	2.5% max.
	Nickel	40 to 60%
	Chromium	30 to 40%
	Molybdenum	3.0% max.
30	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	1.0% max.
	Zirconium	1.0% max.
	Cobalt	2.0% max.
35	Tungsten	1.0% max.,

Aluminium 0 - 15.0%  
Nitrogen 0.001 - 0.5%  
Oxygen 0.001 - 0.7%  
balance iron and incidental impurities.

5

6. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.03 to 0.2%
10	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	40 to 50%
	Chromium	30 to 40%
	Molybdenum	3.0% max.
15	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.0% max.
20	Tungsten	1.0% max.,
	Aluminium	0 - 15.0%
	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

25

7. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.3 to 0.7%
30	Silicon	0.01 to 2.5%
	Manganese	2.5% max.
	Nickel	19 to 22%
	Chromium	24 to 27%
	Molybdenum	3.0% max.
35	Niobium	2.0% max

30

	Hafnium	0.01 to 4.5%
	Cobalt	2.0% max.
	Tungsten	1.0% max.,
	Aluminium	0 - 15.0%
5	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

10 8. An alloy according to claim 1 having the following composition, by weight:

	Carbon	0.03 to 0.2%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max
15	Nickel	30 to 45%
	Chromium	19 to 22%
	Molybdenum	3.0% max.
	Niobium	2.0% max.
	Hafnium	0.01 to 4.5%
20	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.
	Aluminium	0 - 15.0%
25	Nitrogen	0.001 - 0.5%
	Oxygen	0.001 - 0.7%
	balance iron and incidental impurities.	

30 9. An alloy according to any one of claims 1, 2, 3, 5, or 7, having a carbon content of from 0.3 to 0.5% by weight.

10. An alloy according to claim 1 or 2, having a carbon content of from 0.03 to 0.2% by weight.

35

11. An alloy according to claim 1, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.01 to 3.0%.

5

12. An alloy according to claim 11, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.

10

13. An alloy according to claim 11 or 12, in which the amount of carbon in the alloy, by weight, is from 0.3 to 0.6% and the amount of hafnium in the alloy, by weight, is from 0.2 to 0.5%.

15

14. An alloy according to any one of the preceding claims, in which the amount of carbon in the alloy, by weight, is from 0.03 to 0.2% and the amount of hafnium in the alloy, by weight, is from 1 to 4.5%.

20

15. An alloy according to any one of claims 1 and 4 to 8, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 10% and the amount of hafnium by weight is from 0.01% to 4.5%.

25

16. An alloy according to claim 15, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 6% and the amount of hafnium by weight is from 0.1% to 1.0%.

30

17. An alloy according to claim 15 or 16, in which the amount of aluminium in the alloy, by weight, is from 0.1% to 4.5% and the amount of hafnium by weight is from 0.2% to 0.5%.

35



18. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less.

19. An alloy according to any one of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 5 microns to 0.25 microns, or less.

20. An alloy having any one of the following compositions, by weight:

15

Carbon	0.45%
Silicon	1.3%
Manganese	0.9%
Nickel	33.8%
Chromium	25.7%
Molybdenum	0.03%
Niobium	0.85%
Hafnium	0.25%
Titanium	0.1%
Zirconium	0.01%
Cobalt	0.04%
Tungsten	0.01%
Nitrogen	0.1%
Iron	balance.

30

Carbon	0.07%
Silicon	1.0%
Manganese	0.98%
Nickel	32.5%
Chromium	25.8%

35

	Molybdenum	0.20%
	Niobium	0.04%
	Hafnium	1.1%
	Titanium	0.12%
5	Zirconium	0.01%
	Cobalt	0.04%
	Tungsten	0.08%
	Nitrogen	0.1%
	Iron	balance.
10		

	Carbon	0.34%
	Silicon	1.68%
15	Manganese	1.10%
	Nickel	32.0%
	Chromium	21.3%
	Molybdenum	0.01%
	Niobium	0.80%
20	Hafnium	0.25%
	Titanium	0.12%
	Zirconium	0.01%
	Aluminium	3.28%
	Cobalt	0.04%
25	Tungsten	0.01%
	Iron	balance

	Carbon	0.42%
	Silicon	1.79%
30	Manganese	1.17%
	Nickel	33.2%
	Chromium	23.3%
	Molybdenum	0.02%
	Niobium	0.77%
35	Hafnium	0.24%

	Titanium	0.10%
	Zirconium	0.01%
	Aluminium	1.64%
	Cobalt	0.04%
5	Tungsten	0.08%
	Iron	balance

21. An alloy according to any one of the preceding claims substantially as described in Examples 1 to 4.
22. An alloy according to any one of the preceding claims substantially as described in Example 5.
23. A nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.
24. An oxide dispersion strengthened nickel-chromium-iron alloy which comprises up to about 5% by weight of hafnium, with at least part of the hafnium being present as finely divided oxidised particles.
25. A corrosion resistant nickel-chromium-iron-aluminium alloy comprising up to about 15%, preferably up to about 10%, by weight, of aluminium and up to about 5% by weight of hafnium-containing particles.
26. A method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.
27. A method according to claim 26, in which the alloy

is an alloy as claimed in any of claims 1 to 25.

28. A method according to claim 26 or 27, wherein the hafnium particles have a particle size of less than 50 microns.
29. A method according to any one of claims 26 to 28, in which the amount of hafnium added to the melt is from 0.01 to 3.0% by weight.
30. A method according to any one of claims 26 to 29, wherein the hafnium particles are added to the melt shortly before pouring the molten alloy into a mould.
31. A method according to claim 30, in which the hafnium particles are added to the molten alloy in a ladle.
32. A method according to any of claims 26 to 31, in which the hafnium is electrolytic hafnium.
33. A method according to any one of claims 26 to 32, wherein the level of oxygen in the melt is varied by additions of one or more of niobium, titanium and zirconium.
34. A method according to claim 33, in which the titanium is added in the form of TiFe after the hafnium addition.
35. A method according to any of claims 22 to 32, in which the melt temperature is in the range of from 1500°C to 1700°C.
36. A method of manufacturing a corrosion resistant

nickel-chromium-iron which comprises adding sequentially finely divided hafnium particles and aluminium to a melt of the alloy before pouring.

5 37. A method according to claim 36, wherein the aluminium is added to the melt immediately before pouring the molten alloy into a mould.

10 38. A method according to any one of claims 26 to 37, in which the alloy is formed into a tube by rotational moulding.

15 39. A method according to any one of claims 26 to 38 substantially as described in Examples 1 to 4.

40. A method according to any one of claims 26 to 39 substantially as described in Example 5.

20 41. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium particles to the melt before pouring.

25 42. A creep resistant alloy tube formed from a nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.

30 43. A tube according to claim 42, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.

44. A nickel-chromium-iron alloy tube comprising up to about 5% of hafnium-containing particles substantially as hereinbefore described.

35 45. A tube formed from an alloy according to any of

claims 1 to 25 by rotational moulding.

46. A nickel-chromium-iron alloy having a structure and composition substantially as described and illustrated in any one of Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.
47. A nickel-chromium-iron alloy having a structure substantially as described and illustrated in Figures 5 or 6 of the accompanying Drawings.
48. A corrosion resistant alloy tube formed from a nickel-chromium-iron alloy comprising up to about 15% of aluminium and up to about 4.5% of hafnium-containing particles.
49. A tube according to claim 48, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium.
50. A nickel-chromium-iron alloy tube comprising up to about 5% of hafnium-containing particles substantially as hereinbefore described.
51. A tube formed from an alloy according to any of claims 1 to 25 by rotational moulding.
52. An alloy according to any one of claims 1 to 25, 46 and 47 produced by a method according to any one of claims 26 to 41.

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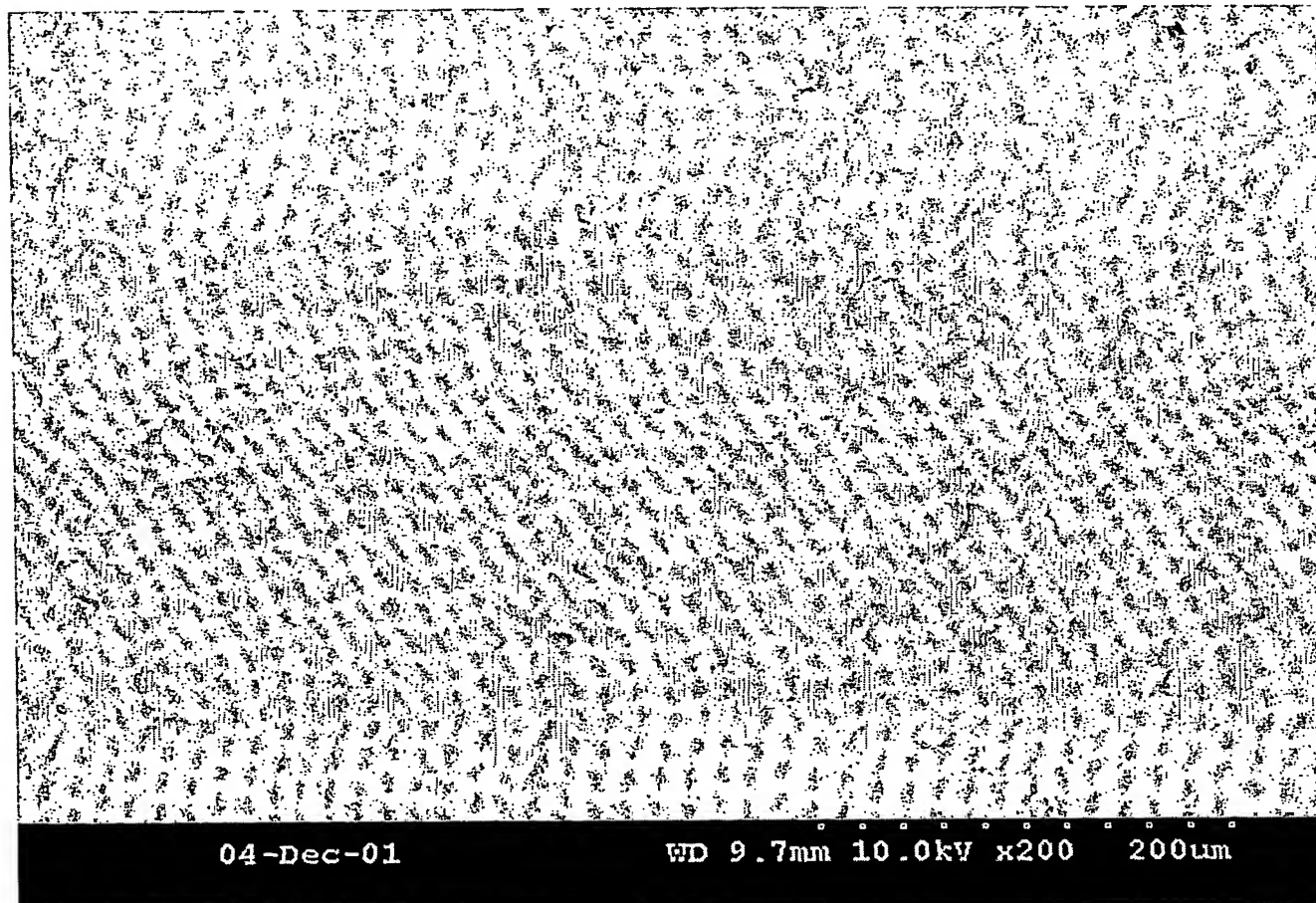


Fig. 1

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.41	1.12	0.73	34.3	25.7	0.02	0.96	0.26	0.00	0.008	0.05	0.01

Traces (Al + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.31

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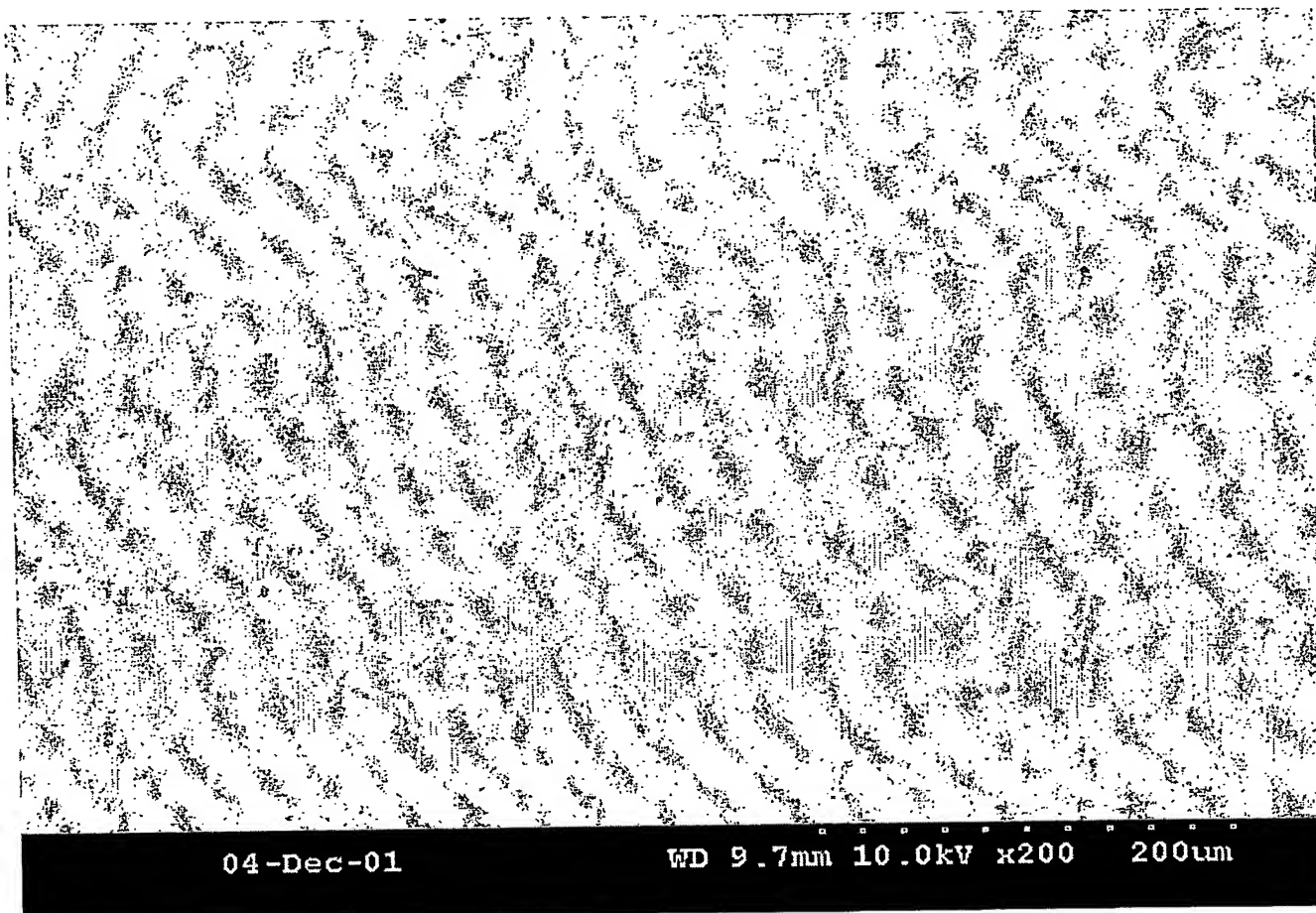


Fig. 2

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.41	1.85	1.47	34.7	24.4	0.05	0.96	0.10	0.09	0.01	0.04	0.02

Traces (Al + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.32



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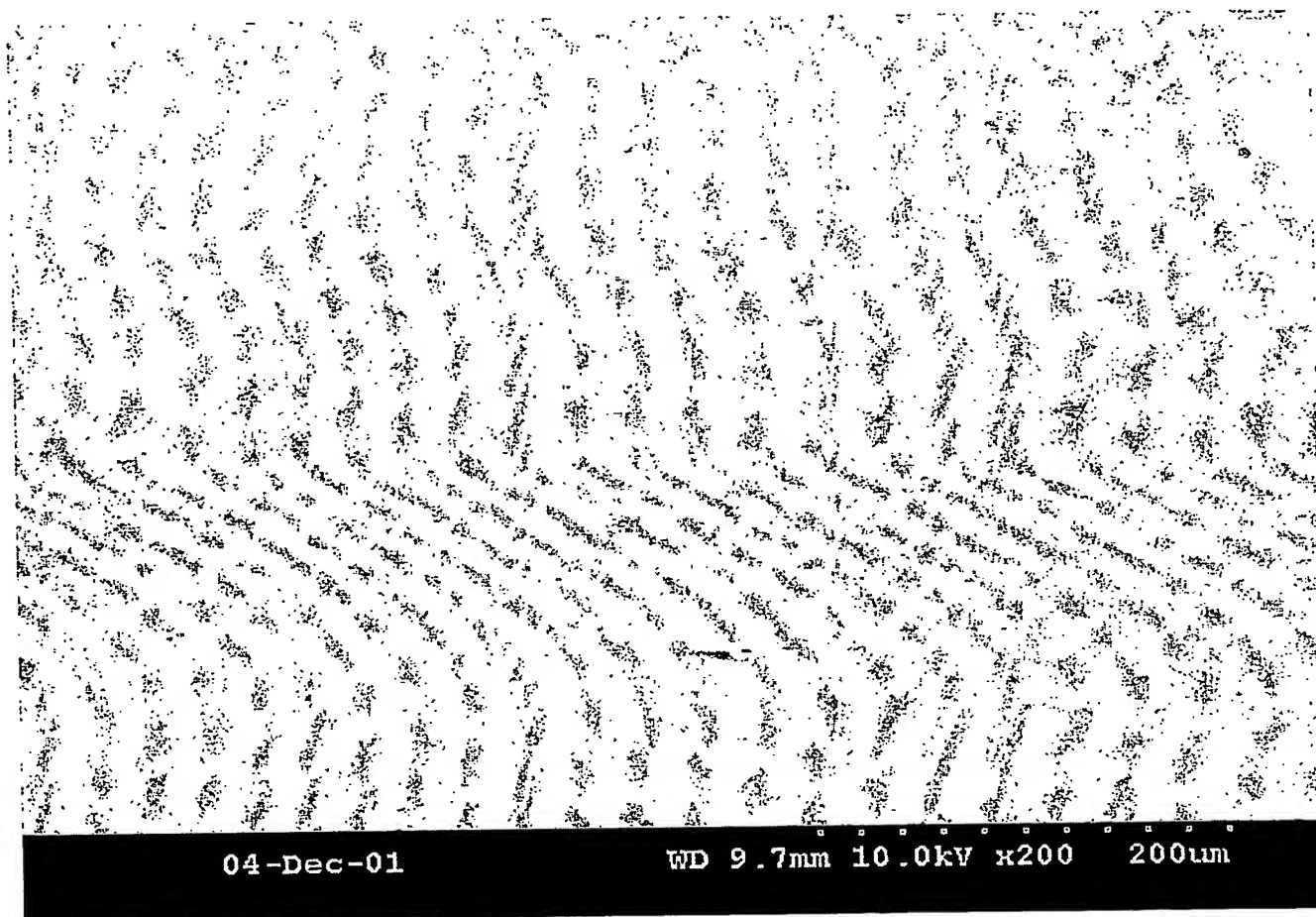


Fig. 3

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.40	1.51	0.96	33.2	24.7	0.02	0.77	0.31	0.08	0.01	0.05	0.01

Traces (Al + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.28

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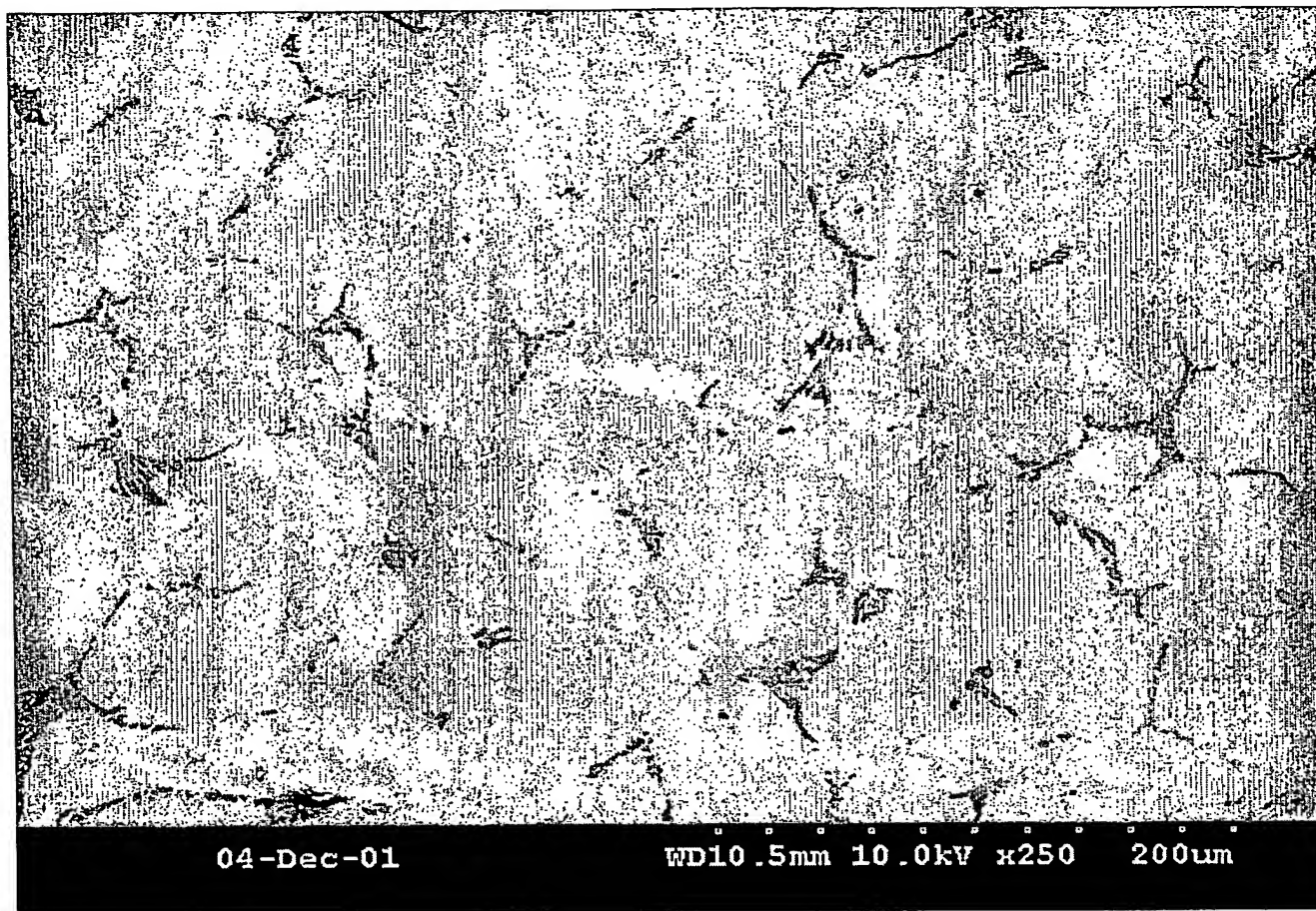


Fig. 4

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.45	1.30	0.90	33.8	25.7	0.03	0.85	0.25	0.10	0.01	0.04	0.01

Traces (Al + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.29

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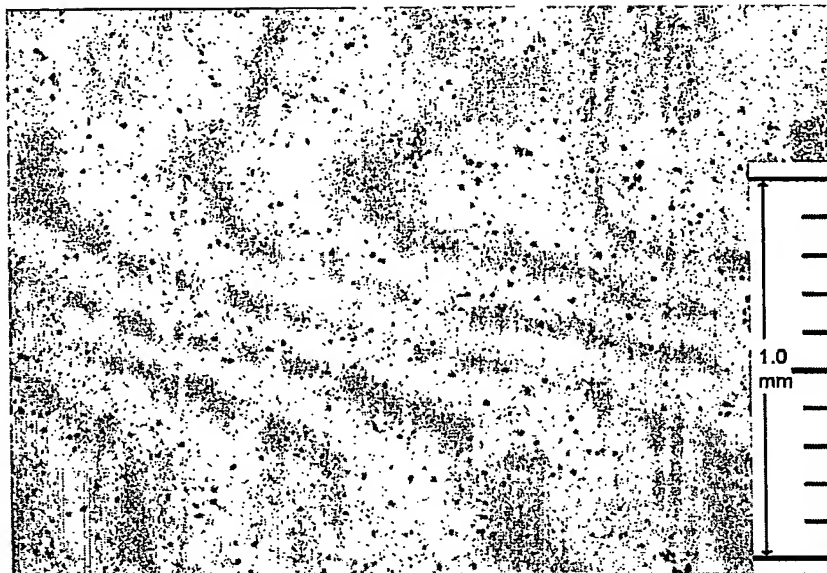


Fig. 5



Fig. 6

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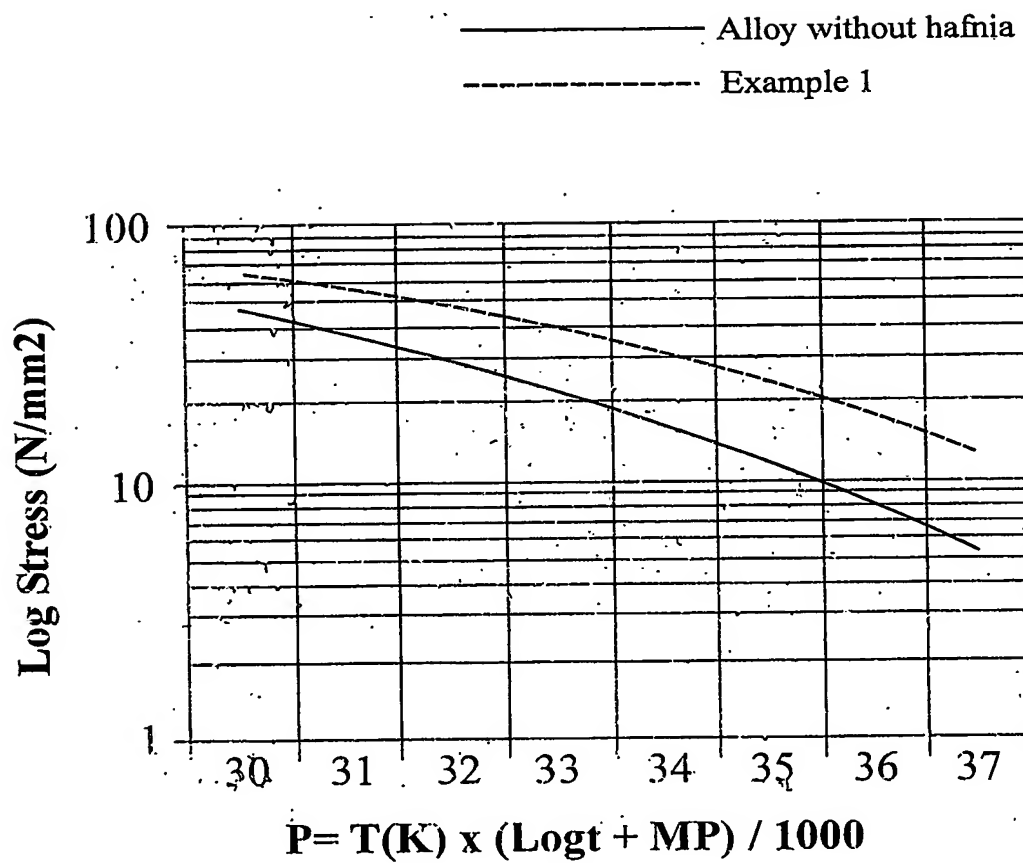
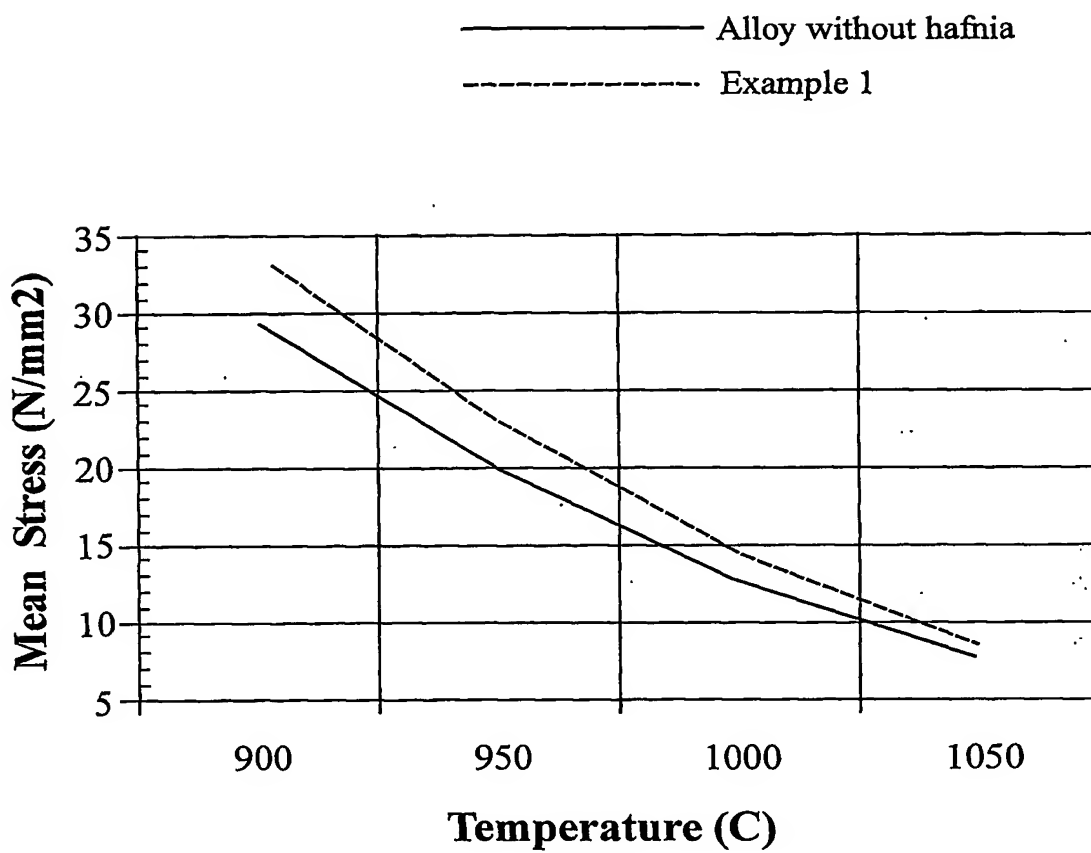
**Larson-Miller Curves**

Fig. 7

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**100,000hrs creep strength comparison****Fig. 8**

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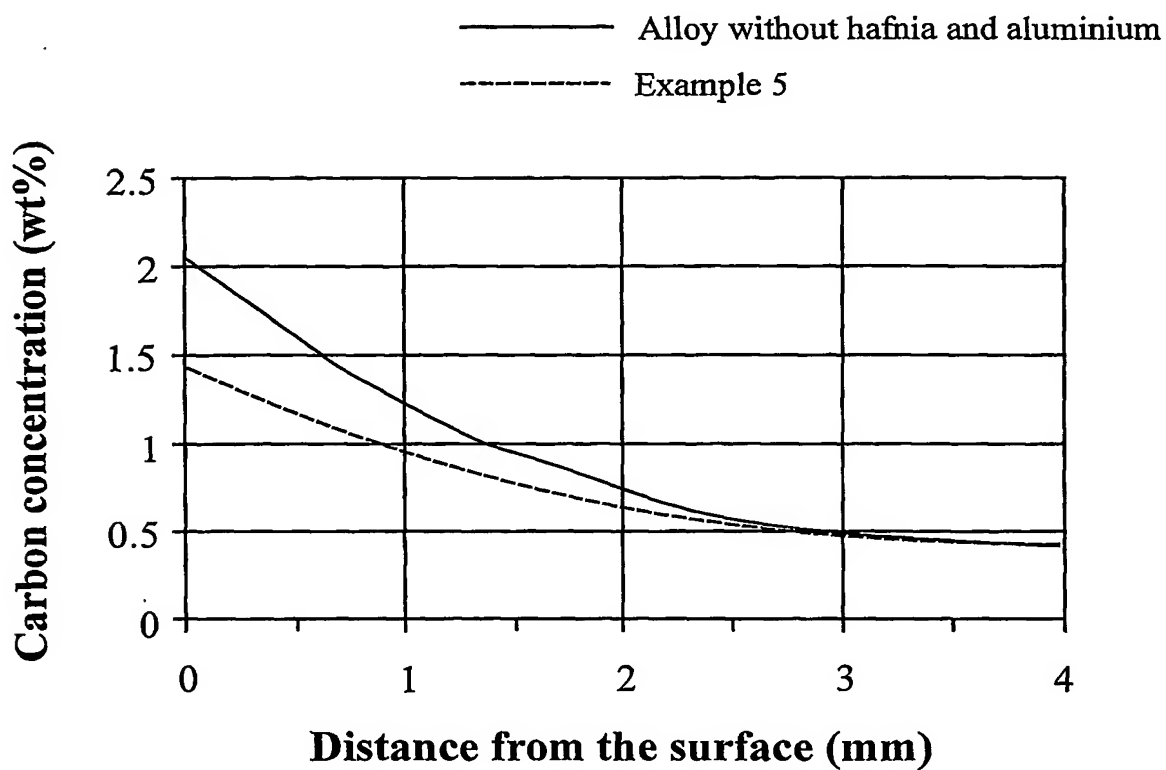
**Pack-Carburisation Test at 1150C During 200hrs**

Fig. 9